

# PATENT SPECIFICATION



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The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act 1949 are Ernst-Guenther Kastning and Klaus Bronstert, citizens of Germany and residents, respectively, of 165 Sternstrasse, Ludwigshafen/Rhein, Germany and 20 Leuschnerstrasse, Ludwigshafen/Rhein, Germany.

## COMPLETE SPECIFICATION

### NO DRAWINGS

#### Improvements in the Polymerisation and Copolymerisation of Alpha-methylstyrene and its Derivatives Substituted on the Nucleus

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a Joint Stock Company organised under the laws of Germany, of Ludwigshafen on Rhine, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

10 This invention relates to a process for the polymerisation and copolymerisation of alpha-methylstyrene and its derivatives substituted on the nucleus.

It is already known that alpha-methylstyrene can be polymerised only with difficulty with radical-forming catalysts. With 15 ionic catalysts, such as aluminium chloride, boron fluoride or titanium-4-chloride, alpha-methylstyrene can be polymerised to liquid to solid brittle products. This polymerisation is markedly dependent 20 on temperature. Solid polymers are only obtained at a polymerisation temperature of about -100°C or less. It is possible to dimerise alpha-methylstyrene with sulphuric acid or phosphoric acid at higher temperatures. It is also known that alpha-methylstyrene can be polymerised with sodium to high molecular weight products. This 25 process is however quite troublesome to carry out because very long polymerisation periods are required, for example 100 to 150 hours or more. Moreover only somewhat more than 50% of the alpha-methylstyrene 30 is polymerised.

We have now found in accordance with the present invention, that alpha-methylstyrene which may be substituted on the nucleus by organic groups non-reactive with the catalysts to be employed can be polymerised and copolymerised advantageously at temperatures between -100°C and +60°C with the aid of alkali metals and/or alkali metal hydrides as catalysts to form 45 high molecular weight polymers or copolymers by carrying out the polymerisation in the presence of cyclic ethers or acetals.

Derivatives of alpha-methylstyrene substituted on the nucleus by organic groups 50 non-reactive with the catalysts employed are for example ortho-, meta- and para-methyl-alpha-methylstyrene, 2,4-dimethyl-alpha-methylstyrene or other dimethyl-alpha-methylstyrenes, para-isopropyl-alpha-methylstyrene or also para-vinyl-alpha-methylstyrene and para-isopropyl-alpha-methylstyrene.

The polymerisation commences immediately after the components taking part in 60 the polymerisation have been brought together and then often proceeds so violently that the polymerisation vessel must be cooled. It is ended in about 10 minutes to about 15 hours depending on the degree of dispersion of the alkali metal or the corresponding hydride and the temperature used, and at room temperature it proceeds to a conversion of about 70%. Below 0°C, the conversion is more than 90% and at -20°C 70 is practically complete.

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The alpha-methylstyrene which may be substituted on the nucleus by organic groups non-reactive with the catalysts employed is preferably used immediately after it has been distilled. If it contains impurities, for example autoxidation products, it is true that the polymerisation still takes place, but more catalyst is required and polymers are obtained with somewhat lower molecular weights. Sodium, potassium and also lithium are especially suitable as alkali metals. Mixtures or alloys of these metals with one another may also be used.

The hydrides of sodium or potassium are especially suitable as alkali metal hydrides, but lithium hydride may also be used. Mixtures are also suitable, as are also complexes of alkali hydrides and hydrides of beryllium, magnesium, calcium, strontium, barium, boron aluminium, gallium, indium and thallium, as for example  $\text{Na}(\text{AlH}_4)$ .

Tetrahydrofuran and dioxane are examples of suitable cyclic ethers in the presence of which the polymerisation is to be carried out. Suitable acetals are for example acetaldehyde dimethyl acetal, acetaldehyde diethyl acetal or other acetals of aliphatic aldehyde with aliphatic alcohols, and also benzaldehyde dimethyl acetal. Mixtures of cyclic ether with the acetals may also be used. During the polymerisation process, the cyclic ethers and acetals not only serve to accelerate the polymerisation but they act at the same time as diluents so that the reaction mixture can be moved and stirred and a good thorough mixing of the components participating in the polymerisation and also a good withdrawal of the polymerisation heat can be achieved. In different hydrocarbons, as for example pentane, hexane, octane, benzene and toluene may also be used as additional diluents. By continually moving the reaction medium it is possible to lead away the polymerisation heat well so that the constancy of temperature is ensured.

The polymerisation may also advantageously be carried out in screws or kneaders. This is especially preferable when the polymerisation is carried out continuously. When polymerising in screws or kneaders, an intimate mixing of the polymerisation components takes place even when the polymerisation mixture has become very viscous and tough in an advanced stage of

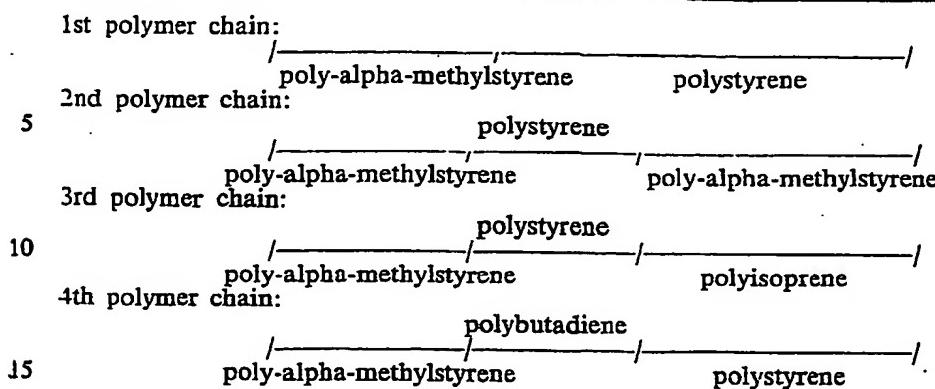
the polymerisation. A liquid medium is of advantage for working up because by pouring into an alcohol, as for example methanol, ethanol or propanol, or into water while stirring vigorously, the poly-alpha-methylstyrene is obtained directly as a white powder in the pure state. The catalyst is thereby washed out and remains in the washing liquid when the polymer is separated. The removal of the catalyst from a solid reaction medium is more difficult.

The polymer may also be worked up with water or steam or in a kneading machine in the presence of air. The end groups of the polymer occupied by sodium are thereby oxidised and polymeric alcoholates are obtained which can remain in the polymer and are effective therein as lubricants.

A special peculiarity of the process resides in the fact that after the polymerisation of a given amount of alpha-methylstyrene has ended, the polymerisation can be continued by the addition of fresh alpha-methylstyrene, even after a prolonged interruption of up to several days. In this way the molecular weight of the polymer originally present is increased, i.e. the newly introduced monomers polymerise onto the already formed polymers. In this way the molecular weight can be adjusted at will. An upper limit is provided in practice by the fact that the polymerisation proceeds more sluggishly with increasing dilution. For example poly-alpha-methylstyrenes with limiting viscosities above about 3 are formed only after very long reaction periods (up to 100 hours) whereas polymers with limiting viscosities up to 2 form by a rapid reaction.

A polymerisation which has already taken place can be continued not only with alpha-methylstyrene but also with other monomers, as for example with styrene or nuclear alkylated styrenes, or with dienes, as for example butadiene or isoprene, or with vinylcarbazole. The polymerisation may also be continued consecutively with two or more of these monomers or also with alpha-methylstyrene.

There are thus formed copolymers in which the components of the copolymer are not distributed statistically in the polymer chain, but in which large sections of the polymer chain consist of one component. For example copolymer chains may be built up from the following components:



The copolymers thus prepared are linear graft polymers in contrast to graft polymers which are prepared for example by grafting an irradiated polymer and which contain the 20 graft components as side chains.

If, however, one or more of the copolymerisation components are mixed with alpha-methylstyrene and the mixture is polymerised according to this invention, 25 copolymers are obtained which contain the components statistically distributed in the polymer chain.

The copolymers should contain at least 20% by weight of alpha-methylstyrene or a 30 derivative of alpha-methylstyrene.

The linear grafting of a further component onto poly-alpha-methylstyrene renders the polymer very stable thermally, for example up to about 260°C. Pure poly-alpha-methylstyrene, on the contrary, already suffers a 35 marked depolymerisation at this temperature.

Oxygen and water, and also alcohols, must be carefully excluded during the polymerisation. Even small traces of these substances 40 have a troublesome effect, especially when high molecular weights are aimed at, because each of these molecules interrupts a polymerisation chain.

The homo-poly-alpha-methylstyrenes obtained by this process have high mechanical 45 resistance and stability to high temperature. They soften between 160° and 173°C. They have excellent dielectric properties and may serve for the production of electrical insulating members resistant to elevated temperatures.

Graft copolymers of poly-alpha-methylstyrene with styrene are of special technical 55 interest because they are boil-proof and capable of being sterilised, i.e. they are not softened or attacked by boiling water and may even be allowed to come into contact with superheated steam without being affected. The softening point of these graft 60 polymers is higher than that of the copolymers of the same composition; for example a copolymer from 22.5% of alpha-methylstyrene and 77.5% of styrene softens

at 108°C, whereas a graft copolymer of the same composition does not soften until 65 113°C.

The following Examples will further illustrate this invention but the invention if not restricted to these Examples. The parts are parts by weight and all the k-values 70 (according to Fikentscher, Cellulosechemie, volume 13, 58 (1932)) are measured in 1% toluene solution.

#### *Example 1*

100 parts of freshly distilled alpha-methyl- 75 styrene, 50 parts of dry tetrahydrofuran and 0.5 part of sodium cuttings are stirred at 25°C under nitrogen in a stirring vessel. After about 10 minutes, the metallic sodium dissolves and the polymerisation starts with 80 a red colouration of the reaction mixture. The heat of reaction is withdrawn by external cooling. After a total of about 30 minutes, the polymerisation is ended. The very viscous reaction product is introduced 85 into methanol with vigorous stirring and the poly-alpha-methylstyrene thereby separates as a white powder. This is washed with methanol and dried in vacuo at 100°C. 77 parts of poly-alpha-methylstyrene are ob- 90 tained having a k-value of 46.5 and a softening point of 165°C. In the case of an identical batch but in the absence of tetrahydrofuran, no polymerisation takes place even after 100 hours. 95

#### *Example 2*

150 parts of tetrahydrofuran are added a little at a time to 236 parts of alpha-methylstyrene and 1 part of sodium powder at 20°C, while stirring. After the first 10 parts of 100 tetrahydrofuran have been added, the polymerisation commences with strong evolution of heat and the polymerisation vessel is cooled externally. As the reaction mixture thickens, the remaining portions of tetrahydrofuran are added so that the mixture can be stirred well up to the end of the polymerisation. The polymerisation is ended after 45 minutes. The reaction mixture is washed with ethanol. 191 parts of poly- 105 alpha-methylstyrene are obtained having a 110

k-value of 59.2 and a softening point of 169.5°C.

*Example 3*

By working as in Example 2 but using 5 1.5 parts of potassium powder instead of 1 part of sodium powder, only 110 parts of tetrahydrofuran are needed to keep the reaction mixture capable of being stirred well until the end. The polymerisation is 10 ended after 4½ hours. After working up as in Example 1, 158 parts of poly-alpha-methylstyrene are obtained with a k-value of 42.2 and a softening point of 162°C.

*Example 4*

15 200 parts of alpha-methylstyrene are rolled in a rolling vessel with 5 parts of tetrahydrofuran and 0.3 part of sodium chips at 10°C for 3 hours. During this time the sodium passes into solution and the 20 reaction mixture becomes highly viscous. After standing for another 12 hours at 10°C, the contents of the vessel harden completely. The reaction mixture is ground with methanol to a powder which for purification 25 is then boiled up with methanol and subsequently washed. 174 parts of poly-alpha-methylstyrene are obtained with a k-value of 72.3 and a softening point of 171°C.

*Example 5*

30 100 parts of alpha-methylstyrene are polymerised with 0.5 part of sodium chips and 50 parts of tetrahydrofuran at 25°C as in Example 1. 5 hours after the end of the polymerisation, 500 parts of alpha-methylstyrene are added. After thorough mixing, the polymerisation recommences and intensive cooling with water is necessary to keep the reaction temperature at 25°C. In order to be able to stir the reaction mixture, 350 40 parts of tetrahydrofuran are added a little at a time. After working up as in Example 1, there are obtained 422 parts of poly-alpha-methylstyrene with a k-value of 62 and a softening point of 170°C.

*Example 6*

45 50 parts of alpha-methylstyrene are polymerised at 0°C in the presence of 50 parts of tetrahydrofuran and 0.05 part of sodium chips. When the polymerisation has commenced after about 15 minutes, a further 50 250 parts of alpha-methylstyrene are added a little at a time so that the reaction mixture remains capable of being stirred. After 2 hours, all the alpha-methylstyrene has 55 been introduced and after another hour the mixture can no longer be stirred by reason of the high viscosity. After another 10 hours the reaction mixture, which has become very stiff, is ground to a white powder with 60 methanol. 175 parts of poly-alpha-methylstyrene are obtained with a k-value of 78 and a softening point of 173°C.

*Example 7*

65 100 parts of alpha-methylstyrene are polymerised at -30°C in the presence of 100

parts of tetrahydrofuran and 0.05 part of sodium powder. The polymerisation noticeably commences about 20 minutes after the components have been brought together and ceases after about 60 minutes. After another 70 12 hours, the reaction mixture is worked up with methanol. 96.5 parts of poly-alpha-methylstyrene are obtained with a k-value of 83.5 and a softening point of 171°C.

*Example 8*

75 100 parts of alpha-methylstyrene are polymerised as in Example 1. After the end of the polymerisation, the mixture is diluted with 200 parts of toluene and during the 80 course of 4 hours a mixture of 300 parts of styrene and 300 parts of toluene is added while stirring and with strong external cooling. The temperature is kept at 30°C. After a further hour, half of the reaction mixture is worked up with methanol. 174 parts of a graft polymer with a softening point of 113.5°C are obtained which consists of 22.5% of alpha-methylstyrene and 77.5% of styrene and has a k-value of 57.

To the other half of the reaction mixture 90 another 50 parts of alpha-methylstyrene are added and polymerisation continued at 20°C. After 10 hours, the almost solidified reaction mixture is ground with methanol to a white powder. After purification, 198 95 parts of polymer with a k-value of 61.5 remain behind.

*Example 9*

100 100 parts of alpha-methylstyrene are stirred with 50 parts of acetaldehyde 100 dimethyl acetal and 0.5 part of sodium powder at 25°C for 12 hours. The reaction mixture which has become viscous is then introduced into 500 parts of methanol with good stirring. The white powder which separates out is filtered off by suction, washed with 1% aqueous hydrochloric acid and then with water and dried. The k-value of the poly-alpha-methylstyrene is 48 and the softening point 164.5°C.

*Example 10*

110 80 parts of para-isopropyl-alpha-methylstyrene are stirred for 8 hours at 15°C with 30 parts of tetrahydrofuran and 0.1 part of sodium powder. After working up the 115 reaction mixture with methanol, there remain 53 parts of powdery poly-para-isopropyl-alpha-methylstyrene of the k-value 37.5.

*Example 11*

120 1,500 parts of alpha-methylstyrene and 50 parts of tetrahydrofuran are kneaded with 1 part of sodium powder at 10°C in a kneader. The contents have become highly viscous within 45 minutes. 2 parts of butanol are then kneaded in and the catalyst thereby destroyed. Then the mixture is heated in vacuo at 190°C for 30 minutes. The solvent and unreacted alpha-methylstyrene are thereby removed. The fused poly-alpha- 125 130

methylstyrene is then removed from the kneader through a heated pipe under a pressure of 2 atmospheres. It has a k-value of 60.5 and a softening point of 161°C.

**Example 12**

5      4,000 parts of freshly distilled alpha-methylstyrene are mixed under nitrogen with 2,000 parts of tetrahydrofuran. 2 parts of finest powdered sodium are added there-

10 to. After about 5 minutes the reaction commences with red colouration and is ended after about 60 minutes. The reaction temperature is kept at 10°C by external cooling. While cooling and stirring, 1,000 parts of

15 freshly distilled styrene are dripped in in the course of 3 hours. 30 minutes after the last of the styrene has been added, the reaction is ended by the addition of 100 parts of methanol. The viscous reaction

20 mixture is then kneaded with 10,000 parts of methanol for 45 minutes in a kneader. A white powder is obtained which is washed with water until neutral. The yield is 2,410 parts. The graft polymer consists of 62% of

25 alpha-methylstyrene and 38% of styrene. It softens at 138°C and has a k-value of 77.1.

**Example 13**

30      500 parts of tetrahydrofuran and 3 parts of finest powdered sodium are added under nitrogen to a mixture of 200 parts of alpha-methylstyrene and 200 parts of styrene, both freshly distilled. After the reaction has commenced, a mixture of 750 parts of styrene, 750 parts of alpha-methylstyrene and 2,500

35 parts of tetrahydrofuran is dripped in in the course of 2 hours. After another hour dry air is led into the reaction mixture for 2 hours at the rate of 50 litres per hour. During the entire duration of the reaction,

40 the reaction temperature is kept at 12°C by cooling. The mixture is finally worked up with methanol as in Example 12. 1,455 parts of a copolymer of 42% of alpha-methylstyrene and 58% of styrene are obtained

45 with a softening point of 130°C and a k-value of 63.8. The dielectric constant is 1.92 and the impact strength is 14.5 kg/cm<sup>2</sup>.

**Example 14**

50      0.8 part of finest powdered sodium is added at -20°C to a mixture of 100 parts of styrene and 500 parts of tetrahydrofuran while stirring well and cooling intensely. The reaction vessel is rinsed with nitrogen. The reaction commences after a few minutes and

55 the temperature rises to 10°C. 300 parts of alpha-methylstyrene are then added at once, thoroughly well mixed and the temperature kept at 10°C. The reaction is ended after 45 minutes. Then in the course of 30

60 minutes, another 100 parts of styrene are added. 1 hour after the last of the styrene has been added, the reaction is ended by the addition of 20 parts of methanol. The mixture is kneaded with 1,500 parts of methanol

65 until the polymer is present in powder form.

436 parts of a block graft polymer are obtained which contains 54% of alpha-methylstyrene and 46% of styrene and has a k-value of 68.4.

**Example 15**

70      100 parts of alpha-methylstyrene are polymerised as described in Example 1. After the polymerisation is ended, 15 parts of highly purified isoprene in admixture with 100 parts of tetrahydrofuran are dripped in in the course of 30 minutes while stirring and the reaction temperature kept at 25°C by external cooling. The mixture is then kneaded in 200 parts of ethyl alcohol to a white powder which is filtered off by suction and washed with water until neutral. 96.5 parts of a block copolymer are obtained which contains 16% of isoprene and 84% of alpha-methylstyrene. It softens at 142°C and has an impact strength of 32 kg/cm<sup>2</sup> and

75 a k-value of 59.7.

**Example 16**

80      While excluding oxygen and moisture, 100 parts of pure alpha-methylstyrene and 40 parts of dry tetrahydrofuran are mixed with

85 5 parts of a 20% suspension of sodium hydride in paraffin oil. This reaction mixture is stirred at 25°C. After about 15 minutes, polymerisation commences and the reaction mixture discolours. After another

90 60 minutes, the conversion amounts to about 29%. After 10 hours a conversion of 69.5% has been reached and the reaction mixture is introduced into methanol with vigorous stirring, poly-alpha-methylstyrene

95 thereby separating as a fibrous white powder. It is washed with methanol and dried in vacuo at 100°C.

The k-value of the poly-alpha-methylstyrene is 68.5 and the softening point lies

100 at 167°C.

In an identical batch, no polymerisation has taken place even after 150 hours in the absence of tetrahydrofuran.

**Example 17**

110      500 parts of alpha-methylstyrene are stirred with 100 parts of tetrahydrofuran and 3 parts of finely powdered sodium hydride. When polymerisation has commenced, 400 parts of toluene are added at the rate at which the reaction mixture thickens, so that the contents of the vessel remain capable of being stirred well. The temperature is kept at 5°C by external cooling. After a total of 20 hours, the reaction mixture is poured into 4,000 parts of ethanol with vigorous stirring. The precipitated white fibrous powder is filtered off by suction, boiled up with ethanol once more and then dried in vacuo at 100°C. 452 parts of

115 poly-alpha-methylstyrene are obtained with a k-value of 86.7 and a softening point of

120 172°C.

**Example 18**

125      50 parts of alpha-methylstyrene are stirred

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with 50 parts of tetrahydrofuran and 5 parts of a 20% suspension of sodium hydride in paraffin oil at -30°C. After 28 hours an orange-coloured viscous reaction mixture has formed which has 200 parts of methanol added to it at -30°C. The polymer separates at first in a rubberlike form and gradually disintegrates to a white powder. After purification, 48.8 parts of poly-alpha-methylstyrene are obtained with a k-value of 54 and a softening point of 166.5°C.

*Example 19*

25 parts of di-isopropyl ether and 0.5 part of finely powdered sodium hydride are added to 50 parts of alpha-methylstyrene and stirred at 20°C. After 16 hours, the contents of the vessel have become so viscous that the stirring must be discontinued. After a total of 24 hours, the reaction mixture is ground to a powder with methanol. After purification, 36 parts of poly-alpha-methylstyrene are obtained with a k-value of 66.4 and a softening point of 168°C.

*Example 20*

25 500 parts of alpha-methylstyrene are polymerised as in Example 17. After about 20 hours, the polymerisation is ended. While stirring at 5° to 15°C, 125 parts of styrene mixed with 125 parts of toluene are added 30 to the reaction mixture in the course of 2 hours. After another 4 hours, the reaction product is worked up with methanol and purified. 524 parts of a linear graft polymer of 77% of alpha-methylstyrene and 23% of 35 styrene are obtained with a k-value of 62 and a softening point of 133°C.

**WHAT WE CLAIM IS:-**

1. A process for the production of high molecular weight polymers or copolymers of

alpha-methylstyrene which may be substituted on the nucleus by organic groups non-reactive with the catalyst employed wherein alpha-methylstyrene which may be substituted on the nucleus by an organic group non-reactive with the catalyst is 45 polymerised at a temperature between -100°C and +60°C with the aid of an alkali metal and/or an alkali metal hydride as a catalyst and in the presence of a cyclic ether and/or an acetal.

2. A process as claimed in claim 1 wherein the alpha-methylstyrene or derivative thereof is copolymerised with one or more other copolymerisable monomeric compounds.

3. A process as claimed in claim 1 wherein the alpha-methylstyrene or derivative thereof is first polymerised and then the polymerisation is continued with another polymerisable monomer.

4. A process as claimed in any of claims 1 to 3 wherein the alpha-methylstyrene or derivative thereof is used in a freshly distilled condition.

5. A process for the production of polymers or copolymers of alpha-methylstyrene which may be substituted on the nucleus by organic groups non-reactive with the catalyst substantially as described in any of the foregoing Examples.

6. Polymers or copolymers when obtained by the process claimed in any of claims 1 to 5.

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